Volume 38 January, 1952 *Number 1*

Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

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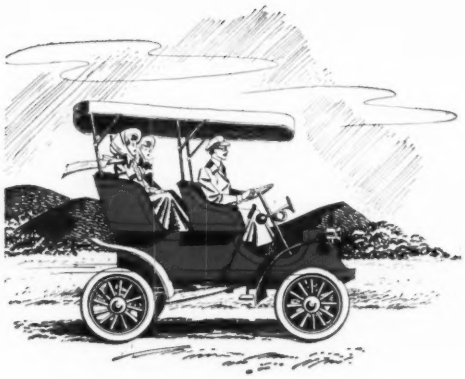
THIS ISSUE

MODERN
AUTOMOTIVE
ENGINE OILS

PUBLISHED BY
THE TEXAS COMPANY
TEXACO PETROLEUM PRODUCTS



MEMORY QUIZ

Quiz yourself on the list alongside. How many of the 200 different makes of gasoline and steam automobiles of fifty years ago can you remember? Only three are still being made today. And in the year 1902, there were only about 9,000 passenger cars produced in the United States. Now, manufacturers turn out more than twice that number *in a single day.*

The automobile and petroleum industries have grown up together. As gasoline superseded steam for automotive power, and cars went into mass production, increasing demands were made on petroleum research to develop better lubricants and fuels and to increase the volume of production.

Texaco has played a leading part in this petroleum research . . . and the goal of all its efforts for half a century has been to make Texaco Products always "first in quality." That is why Texaco Products have won and held the confidence of the American public.

THE TEXAS COMPANY

PASSENGER CARS OF 1902

GASOLINE: ADRIAN ☆ AJAX ☆ AKRON ☆ ALAND ☆ AMERICAN AUTO-DYNAMIC ☆ AUTOMOTOR ☆ BACON ☆ BADGER ☆ BALDNER ☆ BALDWIN ☆ BALZER ☆ BARTHOLOMEW ☆ BEAVER ☆ BERG BINNEY-BURNHAM ☆ BOLTE ☆ BOSTON ☆ BRAMWELL ☆ BRENNER ☆ BRISTOL ☆ BRODESSER ☆ BUCKEYE ☆ BUFFINGTON BUFFUM ☆ BUGGYCAR ☆ CADILLAC ☆ CALIFORNIA ☆ CANDA CANNON ☆ CHELSEA ☆ CHURCH ☆ CHICAGO ☆ CLARK CLARKMOBILE ☆ CLASSIC ☆ CLEVELAND ☆ CLOUCHLEY ☆ COLUMBIA GAS ☆ COVERT ☆ CRESTMOBILE ☆ CUNNINGHAM ☆ DARLING ☆ DAVENPORT ☆ DECKER ☆ DESBERON DETROIT ☆ DURYEA ☆ DYKE ☆ ELMORE ☆ EMPIRE STATE FANNING ☆ FISCHER ☆ FLINT ☆ FRANKLIN ☆ FREDONIA FREEMAN ☆ FRIEDMAN ☆ GASMOBILE ☆ GENEVA ☆ GRANT-FERRIS ☆ GREYHOUND ☆ GURLEY ☆ GYROSCOPE ☆ HALSEY HALSMAN ☆ HALTON ☆ HAMILTON ☆ HAYNES ☆ HEWITT-LINDESTROM ☆ HOLLEY ☆ HOLYOKE ☆ IMPERIAL ☆ INTERNATIONAL ☆ JACKSON ☆ JAMES ☆ JONES-CORBIN ☆ KIBBLINGER ☆ KLOCK ☆ KNOX ☆ KUNZ ☆ LANCASTER ☆ LAW LEACH ☆ LEAR ☆ LEWIS ☆ LOCOMOBILE ☆ LONG DISTANCE LONGEST ☆ LOOMIS ☆ MASSACHUSETTS ☆ MASTER ☆ MEDIA MESSERER ☆ METEOR ☆ MOHLER ☆ MONCRIEF ☆ MOORE MOVER ☆ M.P.M. ☆ MULTIPLEX ☆ MURDAUGH ☆ NEW HOME NEW PARRY ☆ NORTHERN ☆ NORTON ☆ OAKMAN ☆ OGREN OLDSMOBILE ☆ PACKARD ☆ PAN AMERICAN ☆ PAWTUCKET PEERLESS ☆ PEOPLES ☆ PHELPS ☆ PHIANNA ☆ PIERCE-ARROW PIERCE MOTORETTE ☆ PIERCE ☆ PITTSBURGH ☆ POMEROY POPE-HARTFORD ☆ POPE-ROBINSON ☆ POPE-TOLEDO ☆ PRIMO PRINCE ☆ RAMBLER ☆ REAL ☆ REMINGTON ☆ REBER ☆ RED JACKET ☆ RIKER ☆ RIVERIA ☆ ROBINSON ☆ ROCKAWAY ROGERS & HANFORD ☆ ST. LOUIS ☆ SEARCHMONT ☆ SHAIN SHELBY ☆ SKENE ☆ SMITH & MABLEY ☆ SNYDER ☆ SPAULDING SPILLER ☆ STANDARD ☆ STEARNS GAS ☆ STEVENS-DURYEA STRATHMORE ☆ STRONG & ROGERS ☆ THOMAS ☆ THOMSON TRI-MOTOR ☆ TRIUMPH ☆ TWYFORD ☆ UNION ☆ UPTON U. S. LONG-DISTANCE ☆ WALL ☆ WALTER ☆ WARD LEONARD WARWICK ☆ WICK ☆ WILCO SIX ☆ WILDMAN ☆ WINTON WISCONSIN ☆ WOODS MODILLETTE ☆ WORTH.

STEAM: CAPITOL ☆ CHICAGO ☆ CONRAD ☆ COTTA ☆ ECLIPSE ESSEX ☆ FOSTER ☆ GROUT ☆ HENLEY ☆ HOFFMAN ☆ HUDSON KEYSTONE ☆ KIDDER ☆ LANE ☆ LOCOMOBILE ☆ LOZIER MARLBORO ☆ MILWAUKEE ☆ MOBILE ☆ ORIENT ☆ OVERMAN ☆ PRESCOTT ☆ READING ROCHESTER ☆ STANLEY STEAMER ☆ STEAMOBILE ☆ STEARNS ☆ STORCH ☆ TAUNTON WHITE.

TEXACO REG. T.M.

Faithfully yours 1902 | *for Fifty Years* 1952

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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Modern Automotive Engine Oils

WITH the ever increasing use of "additives" in modern automotive oils it appears timely with the opening of a new year to consider once again what "additives" actually are and what are their functions in today's complex heavy-duty type crankcase oils. These are the oils which are complementing advances in mechanical design to give the high efficiency of modern automotive and Diesel Engines.

Going back completely to fundamentals, in order to obtain a proper orientation of the position which addition agents occupy in the crankcase oil performance picture, it is desirable to check on the reasons why a lubricating oil is used in the first place. The *primary* purposes, so classified because failure to meet would lead to rapid engine failure or very unsatisfactory operation, are threefold:

1. to reduce friction (i.e., to lubricate),
2. to act as a coolant and heat transfer medium, and
3. to act as a sealing agent.

The use of addition agents does not contribute significantly to these three primary functions.

The *secondary* functions of lubricating oils are to prevent oil contaminants or deposit forming materials from interfering with engine operation; to prevent rusting of ferrous parts; and to prevent corrosive wear. It is among this secondary group of functions that the limitations of a straight mineral oil appear. Hence it is among this group of functions that chemical addition agents have been used to impart new properties which contribute markedly towards improving the performance of crankcase oils, particularly where heavy duty service is involved.

OIL AND OXIDATION

Today's modern automotive engine oil starts with the selection of a crude oil proven to be most suitable as a raw stock. Even from a selected crude only a part of the hydrocarbons in the proper viscosity range are of suitable chemical structure to meet modern lubrication needs. By the application of modern refining methods, the hydrocarbons unsuitable for lubricating purposes are removed to give the refined base stock for "additive" oils.

Every refined lubricating oil is composed of an almost infinite variety of hydrocarbon molecules. However, for practical purposes it can be considered to be made up of a few basic structural units built around ring type structures as shown in Tables I and II.

Basically, all hydrocarbons are susceptible to oxidation when mixed with air, particularly at elevated temperatures, and in practically all cases the useful life of lubricants is a function of oxidation or some of its side effects. Since oxidation reduces the usefulness of oil over long operating periods, its control is most important and protection against oxidation is the very important function of "oxidation inhibitor" type addition agents.

Oxidation of a hydrocarbon occurs in steps and the initial formation of a hydroperoxide or peroxide

is generally considered to be the key to the oxidation process. Broadly speaking, a hydrocarbon molecule must be activated prior to oxidation; this activation

TABLE I*

Hydrocarbon Class	*Volume, %*
Paraffinic Naphthenes	70
Polycyclic Naphthenes	10
Monocyclic Aromatics	7
Polycyclic Aromatics	13
	100

may be accomplished with relative ease by heat, light, metal ions, or collision with free radicals. Once the hydrocarbon has been activated it will react with the oxygen with the initial formation of a hydroperoxide in a high energy state and usually unstable. On decomposition the hydroperoxide yields additional free radicals, which set up a chain reaction which is the phenomenon that causes oil to oxidize rapidly once oxidation is started. This is sometimes referred to as auto-catalytic oxidation. The maximum oxidation rate is dominated by this peroxide catalyzed reaction and, as might be expected, the ease of oxidation and the characteristic of oxidation products are influenced by the proportion of the basic structural units. Generally speaking, the paraffinic type molecules tend to oxidize towards acids while the naphthenic structures tend to produce condensation of varnish type materials. The over-all picture of oil oxidation may be summarized schematically as follows:

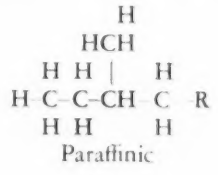
Performance of oil may be impaired by the presence of oxidation products in a number of ways. The peroxide and acidic products acting together may corrode the more reactive metal in bi-metallic or alloy bearings—such as the lead portion of a copper lead bearing. Likewise, the oxy-acids and the aldehydes formed as intermediates during oxidation, when subjected to heat, are capable of condensation and polymerization to complex compounds which are the intermediate steps in the formation of resins, varnish, lacquer and coke-like deposits.

It has been generally observed that below 200°F. a properly refined oil will not oxidize significantly, and above this temperature oxidation will progress, the rate depending upon such factors as the presence of metallic catalysts, soluble metal compounds, water, degree of aeration and temperature and time of exposure. An axiom of chemical reaction generally applicable to non-catalyzed oil oxidation is that the rate doubles for each 18°F. rise in temperature. As will be noted by referring to Figure 1, many parts of an engine in contact with oil are substantially above 200°F. and oil might be expected to oxidize rapidly in areas such as the ring zone where temperatures of 300-600°F. may be reached. However, engine lubrication is dynamic and the constant flow of oil through the lubricating system is an extremely important protecting factor in reducing the hazards of oil oxidation since exposure time at points of highest temperature is usually very short. Actually the crankcase is the place where the bulk of oil is held for maximum time at the operating temperature and for this reason crankcase oil temperature is extremely important in relation to oil deterioration as illustrated in Figure 2.

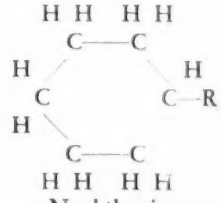
TABLE II

Basic Hydrocarbon Structural Units

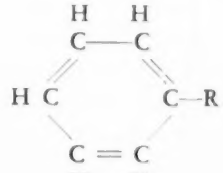
R represents a repetition or combination of the basic units.



Paraffinic



Naphthenic



Aromatic

OXIDATION INHIBITION

The discussion of oxidation inhibition is necessarily complicated since so many types of organic compounds are employed that no one generalization can be made. The most effective and commonly used chemical compounds for oxidation inhibition are

*Hillard, James G., Jones, W. C., and Anderson, Jr., J. A., "Molecular Structure and Properties of Lubricating Oil Components", presented before the Division of Petroleum Chemistry, 119th Meeting, ACS, Cleveland, Ohio, 1951.

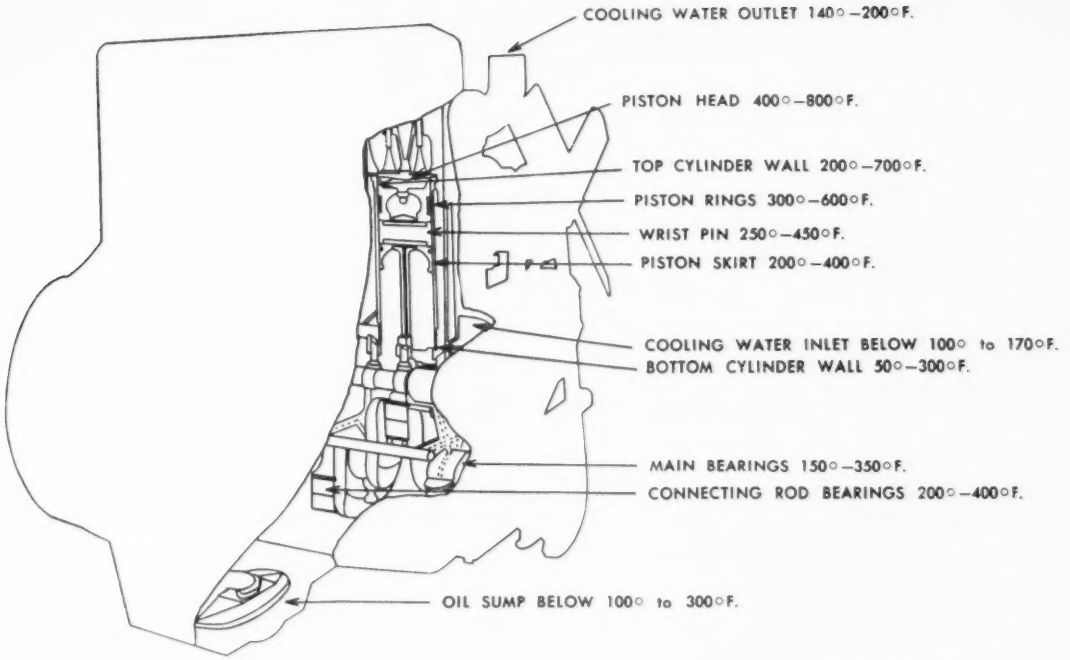

COOLING WATER OUTLET 140°–200°F.
PISTON HEAD 400°–800°F.
TOP CYLINDER WALL 200°–700°F.
PISTON RINGS 300°–600°F.
WRIST PIN 250°–450°F.
PISTON SKIRT 200°–400°F.
COOLING WATER INLET BELOW 100° to 170°F.
BOTTOM CYLINDER WALL 50°–300°F.
MAIN BEARINGS 150°–350°F.
CONNECTING ROD BEARINGS 200°–400°F.
OIL SUMP BELOW 100° to 300°F.

Figure 1 — Some details of a heavy duty automotive type engine showing average temperatures at those points where lubrication is important or where the lubricant might be affected by improper cooling.

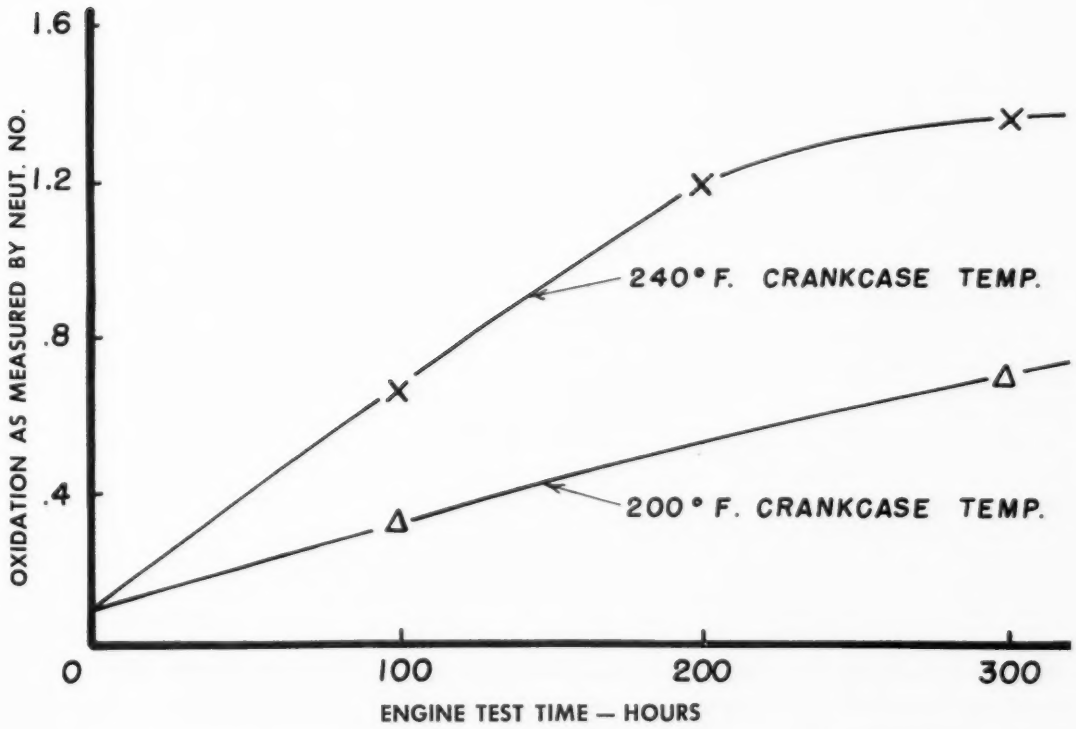


Figure 2 — Effect of crankcase temperature on oil oxidation. Data obtained in railroad type Diesel engine.

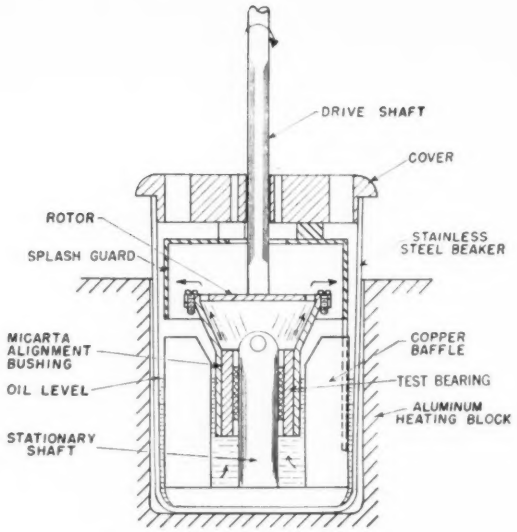


Figure 3 — MacCoull Corrosion Tester.

those containing phosphorus and/or sulfur. As far as the chemical composition of anti-oxidants is concerned, there are so many different types of organic compounds employed that no one generalization can be made. Characteristic functional chemical groups include: thio-ether, di-sulfide, phosphite, phosphate, thio-phosphate, hydroxyl, ester and metal salts in the form of thio-phosphates and thio-carbamates. The mechanism by which these compounds protect oil against oxidation is by no means completely understood. However, four characteristics are usually present: (a) the ability to passivate or inactivate fresh metal surfaces, (b) a deactivating effect on soluble metal compounds that might otherwise promote oxidation, (c) the ability to form an impervious protective film on the bearing surface, and (d) the ability to nullify the action or retard formation of peroxides.

The action of additives to nullify the catalytic effects of metal surfaces and soluble metal compounds is commonly termed catalyst poisoning. At the temperature levels existing in the crankcase, catalytic effects on oxidation predominate. Hence, catalyst poisoning is extremely important in preventing oil oxidation. Catalyst poisoning or passivation of metal surfaces is usually considered to result from the formation of a protective layer or film on the metal surface which may be a physically adsorbed film or a chemical bonding, such as a sulfide coating. The final effect is a rendering of the active catalytic centers on the metal surface inactive for catalytic purposes.

The activity of sulfur or sulfur-phosphorus additives in forming sulfide or similar type coating on ferrous or alloy metal parts varies both with chemical structures and with temperature. While this property is desirable to a degree in poisoning metal surfaces and providing a protective plating on bearings, it must be closely controlled in the development of additive oils otherwise at certain high temperature points, such as exhaust valve guides or at the wrist pin bushings, a deteriorating corrosive action may occur if certain metals are used. The proper balance between catalyst poisoning and any form of sulfide coating tendency is a fine point in additive oil development.

This balance between catalyst poisoning activity and type of sulfide or analogous coating requires special laboratory test equipment such as the MacCoull Corrosion Tester, Figure 3, used to obtain the data in Figure 4. Copper baffles are the metal catalysts used to accelerate the oxidation. The MacCoull Test is particularly useful since the catalytic materials may be varied at will in this test. Likewise long experience has given a good degree of correlation with engine operations allowing this test to be used for screening without the necessity of utilizing much more expensive engine tests.

The action of additives in nullifying the effect of peroxides is normally considered a true "anti-oxidant" effect as differentiated from oxidation inhibition by catalyst poisoning. Since the peroxides play a key role in determining oil oxidation rate under both catalyzed and non-catalyzed conditions, and since their presence is essential in the corrosivity of oxidized oil to bearing metals, the ability of anti-oxidants to nullify their effect is an important characteristic. These materials probably function by reacting with the free radicals formed during decomposition of the peroxide thus limiting or inhibiting the chain reactions which are so instituted and responsible for the so-called auto-catalytic effects which are the most rapid type of oxidation in lubricating oils.

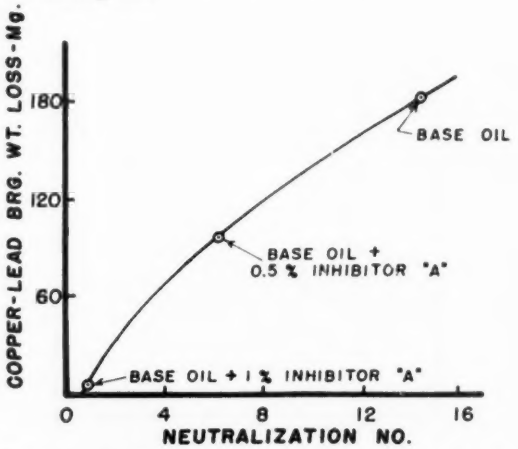


Figure 4 — Effect of a catalyst poison type inhibitor in protecting oil against oxidation and copper-lead bearings against corrosion. Data obtained in MacCouli Test equipment at 350° F. and 10 hr. test period.

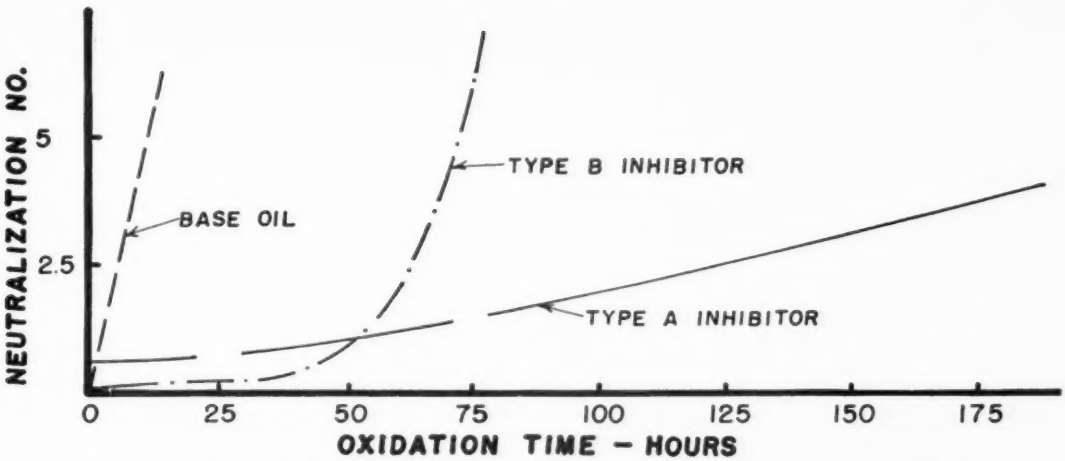


Figure 5 — Results showing Type B inhibitor to be ineffective beyond induction period while Type A inhibitor loses effectiveness very slowly. Results obtained in MacCoull Test equipment at 300°F.

In performing their functions these anti-oxidants themselves undergo a chemical change to a less active or inactive form. This is a phase of inhibiting action that accounts for additive loss and/or reduced protective action with time of service. As might be expected, the degree of permanency of the anti-oxidant effect will vary with the chemical type of inhibitor. This is illustrated in Figure 5 where the oil containing Type B inhibitor oxidizes rapidly once the induction period is passed, while Type A inhibited oil is characterized by a more persistent type of inhibition. For crankcase oils the latter type of inhibition is much preferred.

Various criteria can be applied to measure the effects of oxidation of oil and the protective influence of addition agents. These include determination of acidity, saponification number, viscosity increase, dissolved resins, oil insolubles, varnishing tendency or corrosiveness to alloyed bearings. Figure 4 shows the relationship of acidity and corrosiveness to copper lead bearings as measured in a laboratory test to illustrate the protective effect of an anti-oxidant-catalyst poisoning type of addition agent, while the data in Table III show analogous results obtained in an accelerated laboratory engine test. A visualization of a corroded copper lead bearing, a type of failure directly associated with oil oxidation, is shown in Figure 6.

TABLE III

CRC L-4 Oxidation and Corrosion Test

	Brg. Wt. Loss 36 Hrs.—Gms.	*Neut. No. 16 Hrs.*	*Neut. No. 36 Hrs.*	*CRC Rating*
Reference Oil	5.7	4.2	4.5	82
Same + 0.75% Antioxidant	0.57	0.9	1.3	86
Same + 0.75% catalyst poison	0.12	2.3	3.6	83

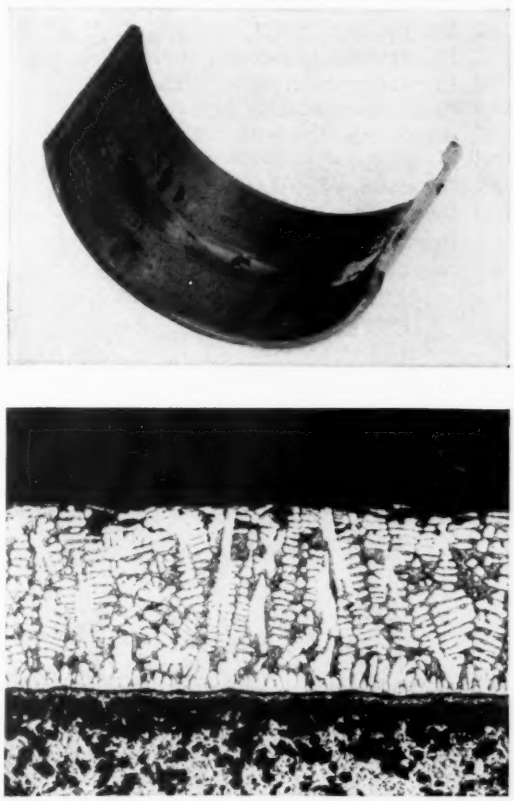


Figure 6 — Top: Corroded copper lead bearing. Bottom: Photomicrograph (100X) of cross section of bearing showing subsurface appearance of corroded area. In this case the lead (grey area) was attacked.

The data of Figure 4 and Table III demonstrate the marked effectiveness of the oxidation inhibitor type of addition agent to protect oil against oxidation and to protect alloyed bearings against corrosion.

DETERGENCY

The ability of an oil to keep an engine free of deposits which interfere with operation has been classified as a secondary function. However, it is extremely important for extended operating periods or for diesel operation where large quantities of soot may result from poor combustion. By usage this characteristic has come to be known as "Detergency" which is a convenient terminology if one broadens the classical definition to include prevention of deposit formation, as well as the purging of undesirable deposits. With this definition of detergency, dispersion is considered a facet of detergency which merely defines the holding of contaminates in suspension regardless of where they are formed. By this broadened definition detergency is associated with the following types of lubrication problems:

1. Preventing piston skirt deposits.
2. Preventing ring sticking.
3. Preventing ring groove deposits.
4. Preventing underpiston deposits.
5. Preventing crankcase deposits.
6. Preventing valve guide and valve stem deposits.
7. Preventing filter plugging.
8. Purging and clean-up of dirty engines.
9. Preventing deposition of all oil insoluble contaminants.

Deposit problems are usually cumulative with operating time but may be aggravated by improper fuel-air ratio, quality of fuel, stop and go operation, and mechanical condition of the engine. Although many test methods have been developed to measure this property they are at best only indicative, and final proof must be obtained in the engine. Probably the most commonly recognized detergency effect is that obtained in diesel engines and the preventive effect of detergent oils on piston deposits in the ring land area is shown in Figure 7. The difference between non-additive and detergent oils is magnified if the sulfur content of the fuel is high. In automotive engines, the principal effect of detergency is noted not only in the piston cleanliness but in the general improvement in the ring belt area and particularly on the oil control rings.

Detergent action normally results in the contaminants which would otherwise be precipitated being carried in suspension in the oil so that parts remain clean and the contaminating materials may be removed when the oil is drained. The useful life of filters has been remarkably improved due to the dispersant and antifluocculant properties of detergent addition agents towards solid contaminants as illustrated in Figure 8.

Under winter conditions where the crankcase oil temperature might be below 140°F., a type of cold engine deposit is formed which, in addition to giving the engine an extremely dirty appearance, can be decidedly harmful to operation as a result of oil ring clogging and oil pump intake screen plugging. This type of deposit is due to contamination of the oil by water and the products associated with partial fuel combustion. This is a type of engine deposit which detergent oils currently available are only partially successful in combating, hence maintenance recommendations previously presented should be depended upon for its control.*

TABLE IV

Laboratory Automotive Engine Test for Oxidation Stability and Deposit Formation

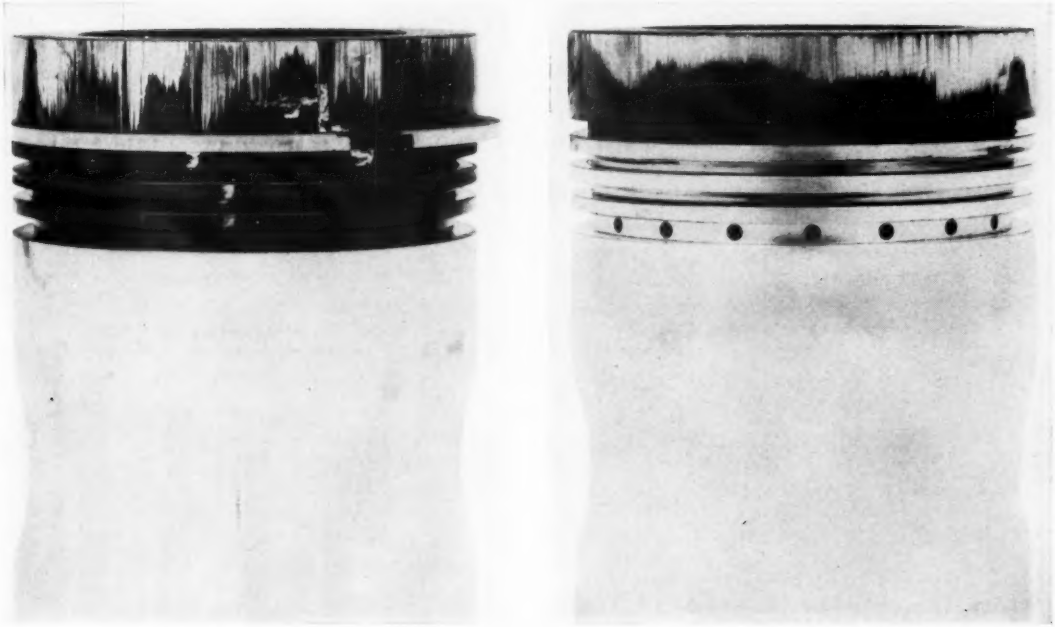
	Neut. No.	*Piston Skirt Deposit, Mgs.*	*Pan and Cover Deposit, Gms.*
Reference Oil	12.5	1250	19.8
Reference Oil + Detergent Additive	9.2	320	4.0

The effect of detergent action under conditions of extensive oil oxidation are shown in Table IV where deposits are markedly reduced with only a minor reduction in oil oxidation. The mode of action in this case is due in part to the effect of the addition agent in promoting the formation of a more soluble oxidation product and in part to a solubilizing action on the oxidized products. In other words, the addition agent directs the course of the oxidation, as well as controlling its extent.

From the illustrations given, it is apparent that detergency as applied to engine cleanliness is a composite of several types of deposit inhibiting actions, each one complex in itself. This probably accounts for the fact that the types of chemical compounds which function most effectively have been discovered mainly by trial and error since their effects are specific to their chemical composition. In general, the chemical compounds which are most effective as detergents and dispersing agents contain a sulfonate, phosphate, phenolate, or carboxylate group, and these are usually combined with a metal such as barium, calcium, magnesium or potassium. Some of the chemical structures involved are illustrated in Table V.

The mechanism by which engine cleanliness is promoted by these addition agents varies with the

*LUBRICATION, Volume 30, No. 12, 1944; Volume 31, No. 11, 1945; Volume 33, No. 2, 1947.



A. Base Oil

B. Base Oil + Detergent Addition Agent

Figure 7 — Effect of detergent addition agent on ring land area cleanliness in single cylinder Diesel Engine Test. Note stuck ring in A. All rings free in B.

A. Base Oil

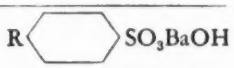
B. Base Oil + Detergent Addition Agent

Figure 8 — Effect of detergent addition agents on filter cleanliness in single cylinder Diesel Engine Test.

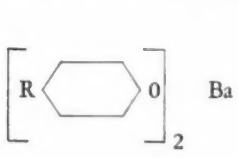
TABLE V

Chemical types of organic compounds which have been extensively used are illustrated by the following chemical structures where R is a hydrocarbon group usually of a paraffinic, or paraffinic-aromatic type.

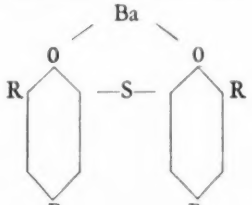
SULFONATE TYPE

$(R\text{-}SO_3)_2Ca$	RSO_3BaOH	
Ca-Petroleum Sulfonate	Basic Ba-Petroleum Sulfonate	Basic Ba-alkylaryl Sulfonate

PHENOLATE TYPE

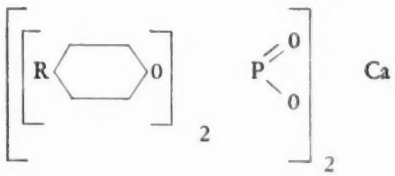


Ba-Alkyl Phenolate



Ba-Alkyl Phenolate Sulfide

PHOSPHATE TYPE



Ca-Alkyl Phenol Phosphate

type of anti-depositant action involved. Properties usually common to these chemical groups and to oils containing them are:

1. they frequently *promote* oil oxidation and appear to act as oxidation directors,

2. they act as de-fluocculating or peptizing agents for insoluble oil contaminants,

3. the more active detergents possess an alkaline reactivity potential, hence may assist in neutralizing acid materials from fuel combustion or oil oxidation,

4. they exert a solubilizing action on oxygenated products (Figure 9),

5. they promote the decomposition of peroxides, as shown in Figure 10.

From this limited review of detergency it appears reasonable to conclude that engine cleanliness is a cumulative effect of both physical and chemical action of addition agents. Likewise, it is apparent that several aspects of detergency are closely related to oil oxidation and the products therefrom. Hence, there exists a close relationship between antioxidants and detergents and as might be expected, a marked complementary effect is frequently obtained with certain combinations of these additive types. The detergent addition agents as a group frequently affect other properties of the oil apart from engine cleanliness, some of them desirable, such as rust protection and corrosive wear protection, and some undesirable, such as foaming and emulsifying action. In each case the effect is the result of the highly polar groups characteristic of these compounds and the trick is to balance the unfavorable characteristics against the benefits derived. In most cases this cannot be done in a single addition agent and consequently combinations of addition agents are generally used.

METAL SURFACE PROTECTION

Such phenomena as rust protection, corrosive wear, extreme pressure characteristics, and erosive wear are associated with the properties of a thin layer of oil at the metal surface, and these in turn are strongly influenced by addition agents that exhibit strong polar characteristics which in effect promote a more tenacious bonding of the oil to the metal surface.

Normally the degree of protection against rusting of cylinder walls, wrist pins and crankshaft bearing surfaces provided by a straight mineral oil is quite adequate for internal combustion engine operation. However, rusting in these areas may become serious in new engines during transit or in storage and to a lesser extent in used engines during long-time storage under humid conditions. Such rusting is caused by droplets of water penetrating the oil layer and attacking the ferrous parts. Special additive type preservative oils are used under severe rusting conditions. However, the heavy duty type oils in general markedly enhance the rust protection afforded by a straight mineral oil as shown in Figure 11.

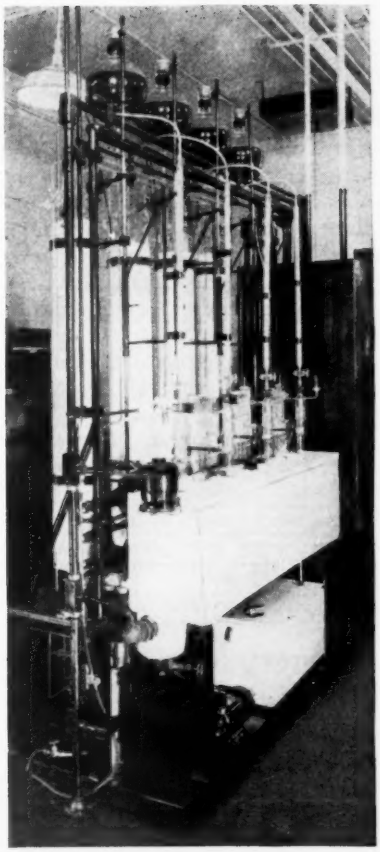


Figure 9A — Glass Multi-Unit Oxidation Equipment used to obtain data in Figures 9 and 10.

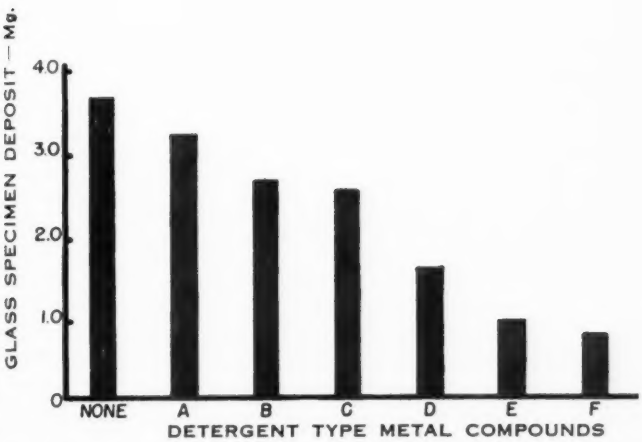


Figure 9 — Solubilizing effect of detergent type metal compounds in reducing the deposition of varnish from a preoxidized oil when heated for 24 hrs. at 338°F. in an inert atmosphere.

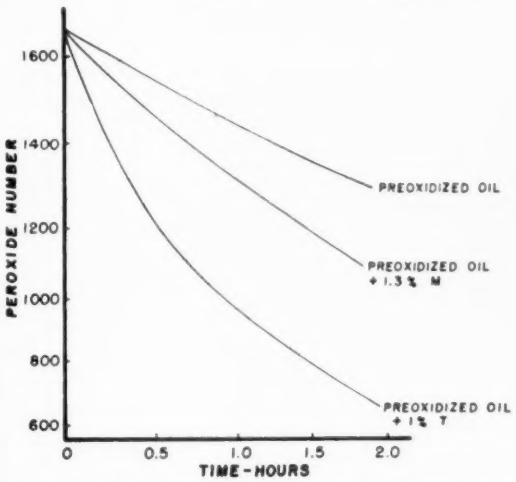


Figure 10 — The effect of detergent type addition agents in accelerating decomposition of peroxides in preoxidized highly refined oil. Temp. 250°F.

Regular Grade Motor Oil

Premium Heavy-Duty Motor Oil

Figure 11 — Modified AN-VV-C-576B Humidity Cabinet Rusting Test.

The protective action is primarily a function of the detergent type addition agents. The mechanism of their action is believed to be due to their polar nature and adsorption at metal surfaces thereby increasing the tenacity with which an oil film is held

to a metal surface thus reducing the possibility of displacement by water.

The phenomenon of low temperature or corrosive wear occurring during the engine warm-up period or during winter operation is generally recognized as being caused by condensation of water vapor from fuel combustion which carries with it acid forming products of fuel combustion in the form of carbon dioxide, organic acids, and inorganic acids; the latter resulting mainly from combustion of leaded or high sulfur fuel. Using cylinder wall temperature as a criterion of engine temperature the results in Figure 12 show the relationship of temperature to corrosive wear.* This type of corrosive wear is another instance where addition agents possessing the chemical characteristics observed for the detergent compounds markedly enhance the protection afforded by a straight mineral oil. This protective action of detergent oils is shown by the ring wear data of Table VI, which was obtained in a laboratory engine operating at 80°F. jacket coolant outlet temperature.

TABLE VI
Corrosive Wear Protection Provided by Detergent Oils

	Per Cent Ring Wear Reduction
Straight Mineral Oil (Reference)	0
Heavy Duty	70
Super Duty	73

The mechanism of low temperature wear protection given by additives is similar to that for rust protection, namely, increasing the tenacity of the oil layer at the metal surface. In addition the alkaline reactivity potential of the more effective compounds tends to neutralize acidity caused by fuel combustion products.

Another facet of crankcase lubrication involving the oil layer at metal surface of moving parts concerns load carrying capacity which as measured by laboratory testing machines is commonly termed "film strength." A straight mineral oil normally provides fluid lubrication with a high safety factor, however, under special conditions such as rapid break-in, using high speed and power output, a critical loading may be attained to such an extent that fluid and boundary lubrication are inadequate, permitting incipient metal to metal contact leading to ring or cylinder wall scuffing. Under these conditions the sulfur, phosphorus or sulfur-phosphorus types of addition agents are beneficial, and the types of these compounds previously discussed in connection with oxidation stability and bearing corrosion protection also contribute a secondary action of increasing "film strength." These additives do not form a ferrous sulfide or phosphate film on the ring or cylinder wall surface at temperatures of normal operation. However, when temperatures rise rapidly at conditions of incipient metal-to-metal contact a metal sulfide or phosphate film may be formed, and thereby provide an increased factor of protection.

*Williams, C. G., "Cylinder Wear in Gasoline Engines," SAEJ. 38, 191, 1936.

COMBINATION OF ADDITION AGENTS

Modern premium, heavy duty and related types of additive oils will commonly contain more than one type of addition agent. In other words, the oil which is finally sold to the consumer is the product of at least two research programs. The first involves the development of the individual addition agents, and the second develops the additive combinations in carefully selected proportions which will give the all-around performance required in the finished oil.

In general, it is not possible to merely combine additives of known properties and obtain a result which is the summation of the properties of the individual addition agents. The additive balance problem is especially complicated where co-related functional properties are involved, such as exist between oxidation inhibitors and detergents. As was previously pointed out, detergent type additives are usually pro-oxidants, and it is essential to use them in combination with an anti-oxidant to obtain a satisfactory level of oxidation stability. This is illustrated in Figure 13, where the base oil plus the detergent oxidizes more rapidly than the base oil alone, but in the presence of an oxidation inhibitor a low level of oxidation, far below that of the base oil, can be maintained.

Likewise, the film forming activity of sulfur or phosphorus-sulfur compounds may be disturbed by detergent additives. Hence, this property also requires careful balancing. In some cases, with high detergent oils, it is necessary to add not only additional anti-oxidant, but also definite catalyst poisoning and film forming materials in order to make the oils both oxidation resistant and non-corrosive to alloy bearings.

The problem of multiple additive types in a single oil is further complicated by what is known as "incompatibility." This may show up in the form of a precipitate during accelerated heating tests or during long-time storage tests, but is usually found at higher temperatures where the additives may chemically react to nullify the good properties of the individual components. Lesser problems are sometimes encountered when pour depressants, viscosity index improvers, or anti-foaming agents are used with oxidation inhibitors and detergents. It can probably be said that combinations of addition

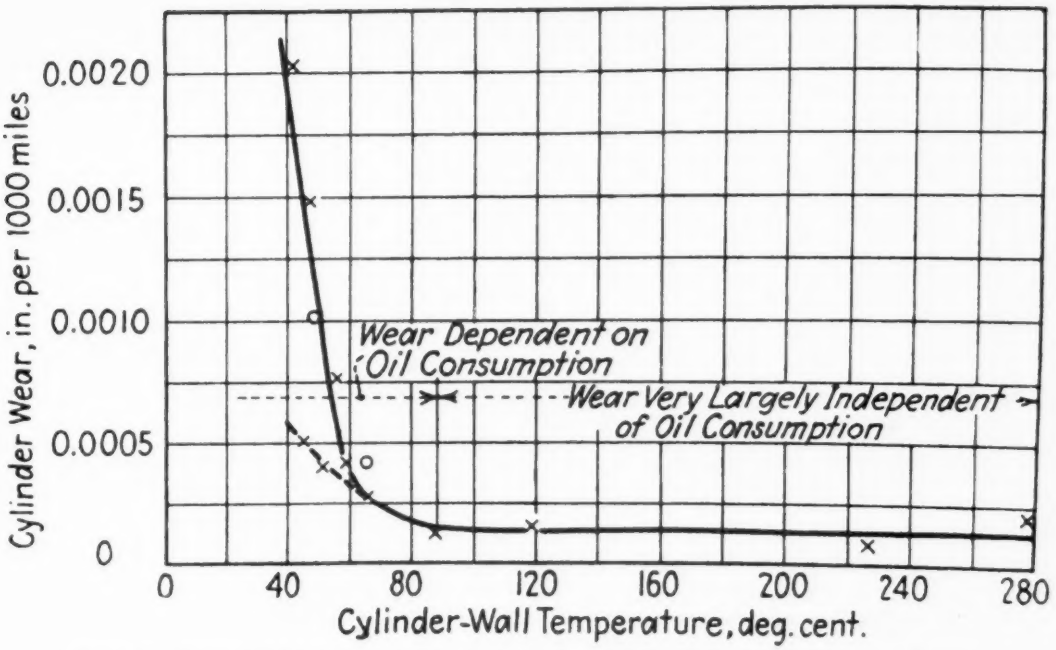


Figure 12 — Courtesy of S.A.E. Journal 38, (5) 191, 1936, C. G. Williams paper on "Cylinder Wear in Gasoline Engines." Cylinder wear in relation to cylinder wall temperature.

agents require more testing than the individual addition agents themselves before they are found to be satisfactory for commercial utilization.

In general, the formulation of a modern heavy duty lubricant requires from two to five years of laboratory and field test work. This does not take into account the background of additive research on which all modern petroleum laboratories depend, and is something which can only be developed by years of painstaking research. It merely means that from the time the decision is made that a new oil is to be developed having certain specific properties, it will be necessary to spend two years or more in the development of the additive combinations, and possibly developing new addition agents, and in finally field testing the products before they are offered to the motoring public.

Testing is normally handled on a laboratory scale and in glass units to eliminate all but the most promising combinations. They then proceed through a series of small scale engine tests, and if they pass are finally tested in full scale laboratory engines under simulated and frequently extremely severe service conditions. If still satisfactory, they are usually road tested in either test fleets or selected customers' equipment. Following this final field test, they are usually introduced in selected areas or to selected accounts for a year or more of service before being put on the market for sale to fleets and individual customers. At the same time extensive evaluation is required for all possible commercial formulations to insure that the material will be stable in storage and that it can be satisfactorily handled and packaged through normal channels to the customer. As might be expected, the development of an improved oil from the initial laboratory experimentation stage to the final field testing of the finished product entails a tremendous outlay of research dollars and time. However, such an expenditure of time and money is most necessary and essential in order to continually translate the research developments of today into the improved products of tomorrow.

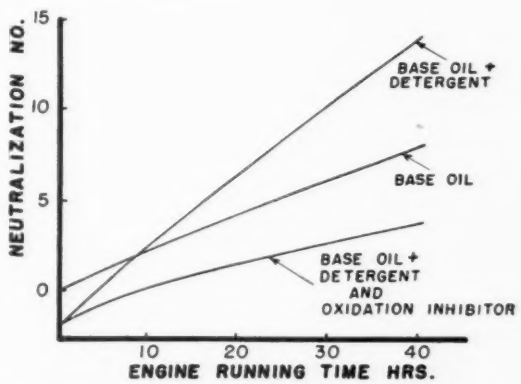


Figure 13 — Results obtained in a multi-cylinder automotive engine with a 300°F. crankcase temperature showing the prooxidant effect of a detergent type addition agent and the response to an inhibitor.

It should be obvious that when additive balance is so particular and the refiners spend so much time and effort on development of these modern motor oils that it should not be necessary to add "improvers" of the type so widely advertised and sold to the motoring public. At best they can add little from a performance angle but they can upset the additive balance and frequently result in poorer performance.

SERVICE CHARACTERISTICS OF ADDITIVE OILS

Used Oil Analysis

Some of the conventional tests applied to used oils may not be applicable to or may require modified interpretation when applied to additive oils. For example the neutralization number test as determined by the ASTM procedure may give a fictitious value with certain metal types of additives. Also due to their dispersant and solubilizing action on oxygenated products the apparent acidity of detergent oils may increase more rapidly during initial operating periods than for a straight mineral oil.

Tests for insoluble contaminants by solubility, blotter, filtration or centrifuging tests also have to be scrutinized carefully. The results may be higher due to the oil picking up more contaminants from the engine or they may be less if determined by centrifuging due to the more finely dispersed nature of the contaminants which prevents complete removal by ordinary clarification techniques.

The use of analytical tests such as ash content, or elemental analysis for metals or phosphorus to indicate quality of used oil is common practice, but definite precautions should be observed. Obviously additive molecules present as oil insolubles would not be considered active yet would be included unless the analytical test is made on carefully clarified samples.

Used oil analyses on additive oils when properly obtained and intelligently interpreted are an invaluable aid to proper operation and maintenance of engine equipment.

Drain Period

Fleet and individual operators have generally become familiar with the fact that detergent type oils become visually dirtier than non-additive oils. This is due to the proper functioning of the addition agents in keeping insoluble contaminants in suspension. Since these contaminants are not readily removed by filters the only way they can be removed from the lubrication system is via oil consumption or periodic oil drain. Allowing an oil to become overloaded with contaminants may result in dropping out of deposits and essential nullification of the purpose for using an additive oil. Careful attention to the observance of proper oil drain period is just as important to additive oils as to non-additive oils.

Additive Life

One of the most recurrent and difficult questions to answer regarding additive oils is the permanency of their action and its relation to frequency of oil drains. From preceding discussions regarding the manner in which addition agents such as oxidation inhibitors and detergents function it is apparent that they themselves undergo certain changes and in a sense are consumed. Hence tests on used oils after clarification or treating with liquid propane will normally show reduction in additive content. The extent of such depletion varies with time in service, type of operation, maintenance practice, and oil consumption. Its relation to service performance is taken into account during the research development of the product by proper selection and concentration of additive components. However, performance in accelerated engine tests or previous experience regarding performance in extended service is in the final analysis essential to confirm the quality and future usefulness of a used oil.

Additive Oils and Combustion Chamber Deposits

With the trend to high compression ratio engines, combustion chamber deposits in spark ignition engines have received considerable attention in connection with octane requirement increase and possible preignition. While these deposits are generally recognized to consist essentially of carbon and lead compounds from leaded fuel it is to be expected that when metal compounds are used in the oil some of the corresponding ash will find its way into combustion chamber deposit as oil escaping past the piston rings is burned. In all cases the additive metal ash found in the combustion chamber deposit is low as compared with lead salts and other combustion products.

CONCLUSION

Additive type crankcase oils are one answer of research to the problem of supplying high quality modern automotive engine oils to meet increasingly severe lubrication requirements and new types of lubrication problems. The trend in recent years has been to turn to the use of these addition agents for the solution to new lubrication problems or to old ones as they become limiting factors to satisfactory lubrication, and it is expected that this trend will continue in the future; hence a basic understanding of additive oil characteristics is a continuing problem. While numerous advantages are realized from their use they never have been nor will be a substitute for the best maintenance practices.

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